

## **Comparative Study on the Extraction of Te(IV) from Various Aqueous Solutions Using Different Organic Diluents and Solvents**

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**Summary.** The extraction of Te(IV) from aqueous solutions containing various ligands has been studied using various inert organic diluents and other solvents. The extraction has been carried out from solutions of different concentrations of HCl, HBr, HI and HNO<sub>3</sub> as well as solutions of the organic acids; citric and oxalic. The used diluents were cyclohexane, carbon tetrachloride, chloroform benzene, p-xylene, toluene and nitrobenzene. The extraction has also been carried out using the following solvents: 20 V% aliquate-336, 20 V% TOA and 30 V% TBP; all in o-xylene to compare with the extraction using inert organic diluents. This extraction study has been carried out to establish the correlation between the distribution of Te(IV) and some physico-chemical properties of the diluents, as well as to provide data with the purpose to find possible economic separation of Te-radioactive isotopes and their daughters, i.e. I-radioactive isotopes, in some extraction systems. Generally, it is found that the increase of distribution ratio of Te(IV) with the studied organic diluents in the most cases of the investigated aqueous solutions has the following sequence: nitrobenzene > CHCl<sub>3</sub> > CCl<sub>4</sub> > p-xylene > benzene > toluene > cyclohexane.

### **Introduction**

Tellurium has some radioactive isotopes that result as fission products in fairly high fission yields. Separation of tellurium radioactive isotopes from aqueous solutions of various compositions such as waste solutions is significant; since they are the parents of iodine isotopes; especially the long-lived isotope <sup>129</sup>I (T<sub>1/2</sub> = 1.57 × 10<sup>7</sup> y). For this reason isolation of tellurium and its concentration from various aqueous solutions such as irradiated uranium solutions, waste solutions and solutions resulting from production of some I-isotopes, beside its separation from associated elements is of great importance. In previous work, Te was separated from other fission products and U in HCl solution using Chelex-100.<sup>(1)</sup> Studies on the extraction of covalent halide complexes of tellurium and some other elements from strong sulfuric acid solutions using non-polar solvents have been carried out.<sup>(2-4)</sup> Studies on the extraction of antimony chloride from solutions of H<sub>2</sub>SO<sub>4</sub> at different concentrations and stripping on

filter paper have also been performed using non-polar solvents.<sup>(5)</sup> The influence of the nature of organic diluents on the extraction of some metal complexes in various systems has been illustrated.<sup>(6,7)</sup> The distribution of metal complexes has been found to be affected with solvent parameters of the diluents such as dielectric constant<sup>(6,8)</sup>, dipole-dipole interaction, donor-acceptor and electrostatic interaction of diluents with the extracted complex,<sup>(9)</sup> Correlation between distribution coefficient and nature of solvents has been also interpreted in the light of change in the activity coefficients of all involved species.<sup>(10)</sup> The principles of all these parameters have been elucidated<sup>(11)</sup> by Y.Marcus.

## Experimental

**Reagents:** All chemicals used were of analytical grade and were products of Merck.

**Radioactive tracer:**  $^{127m}\text{Te}$  ( $T_{1/2}=120\text{d}$ ) was chosen for tracing Te. This isotope was produced via irradiation of suitable compounds of Te in the reactor ET-RR-1 at Inshas. Several other radioactive isotopes were also produced during irradiation of natural Te. The  $\gamma$ -activity of  $^{127m}\text{Te}$  was measured; without any interference from other isotopes; at energy 159 KeV using HPGe multichannel analyzer of 8192 channels, Canberra, USA, with an efficiency 30% at 122 KeV and a resolution of 1.8 KeV at 1332 KeV. The irradiated samples were dissolved in suitable volumes of 6N HCl to form stock solution of Te.

**Procedure:** To measure distribution ratio, batch experiments were performed in stoppered glass tubes by shaking equal volumes (5 ml each) of both pre-equilibrated organic and aqueous phases. The aqueous phase contained suitable aliquot of the irradiated Te solution to give final concentration of Te of  $10^{-3}$  to  $10^{-4}$  mol/L. Extraction was performed at  $30\pm 1^\circ\text{C}$  by shaking in a mechanical thermostatic shaker. Time of 30 min was found to be enough for equilibrium attainment. After a suitable setting period and centrifuging, if necessary suitable aliquot of both phases were withdrawn and assayed by measuring  $\gamma$ -radioactivity. The distribution ratio D is calculated as usual.

Some important physico-chemical properties of the used organic diluents are obtained from literature.<sup>(11-13)</sup>

## Results and Discussion

The Distribution ratios of Te are observed to be independent of the initial Te concentration in the used range ( $10^{-4}$ - $10^{-3}$  mol/L). This indicates the absence of polynuclear species in the studied extraction systems. The obtained D-values at different metal ion activity in both phases remain constant indicating the reversibility of the extraction process.

The extraction of Te(IV) by the used diluents is carried out from the aqueous solutions of HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, oxalic and citric acids. In all cases of the mineral acids the values of D increase with increasing acidity of aqueous phase to reach a maximum which occurs at certain acid concentration and subsequently decrease again. On the other hand, the D-values decrease with the acid concentration in aqueous phase in the case of oxalic and citric acids. At lower acidities the increase in the D-values is attributed to the salting out of the acid, while at higher acidities the decrease is attributed to the competition between the extracted Te-species (in associations) and the acid molecules themselves, which probably takes place at higher acidity. The extraction using these diluents is limited to the transfer of usually unhydrated, undissociated and associated species from an aqueous into an organic phase. Besides at higher concentrations of the used acids Te forms more stable anionic species which remain in aqueous solution.<sup>(14)</sup> The covalent complexes of metals may hydrolyze in organic diluents and aqueous phases depending on the aqueous phase conditions.

In the case of the extraction from citric and oxalic acid solutions, the decrease in the D-values with increasing acid concentration may be attributed to the gradual formation of more stable non-extractable species in the aqueous phase. D-values were evaluated at maximum extraction from the studied aqueous solutions using the investigated organic diluents. D generally decrease in the following order:

a) In the case of organic acids:  $D_{\text{oxalic}} > D_{\text{citric}}$

b) In the case of mineral acids:  $\text{HI} > \text{HBr} > \text{HCl} > \text{HNO}_3$

This may give indication about the stability of the extracted species in the organic phase.

The extraction of Te(IV) depends on the nature of the used organic diluents. The used organic diluents can be categorized into three groups: 1) aliphatic hydrocarbons, 2) aromatic, substituted aromatic hydrocarbons and 3) chloro substituted aliphatic hydrocarbons. Generally, the distribution ratio has the following sequence in the most cases:

nitrobenzene  $>$   $\text{CHCl}_3$   $>$   $\text{CCl}_4$   $>$  p-xylene  $>$  benzene  $>$  toluene  $>$  cyclohexane.

Very poor extraction is achieved in the case of cyclohexane. On the other hand, nitrobenzene is especially efficient in the extraction of Te(IV) in all cases. Among benzene derivatives, extraction apparently changes slightly with increasing number of methyl groups. Similar behavior was observed in a previous work for the extraction of Sb(III) from  $\text{H}_2\text{SO}_4$  with these organic diluents.<sup>(5)</sup> Moreover, it was found that the nature of the diluents has a strong influence on the extraction efficiency of U(VI) by bis(2-ethyl-hexyl)sulfoxide<sup>(7)</sup>, as well as on the formation of TOPO adducts of Eu and Tb Tris- TTA chelates.<sup>(6)</sup> The obtained data show clearly that the distribution ratio of Te(IV) depends on the nature of the investigated diluents. The D-values are generally, higher in the case of solvents with partial polar nature, i.e.  $\text{C}_6\text{H}_5\text{NO}_2$  and  $\text{CHCl}_3$ . This is not unexpected as the protons in these molecules are most likely to form hydrogen bonds or dipole- dipole interaction promoting the solvation of Te(IV) complexes and consequently extraction in the organic diluents. Maxima in extraction are therefore observed in the extraction of Te(IV) to organic phase of polar nature. Polarity of a solvent is dependent on the action of intermolecular forces<sup>(14)</sup>, i.e. coulomb, dielectric, inductive, dispersion and charge transfer forces. Besides, it depends also on polarizability of the diluents molecules, as well as on the solubility parameter. With respect to the polarity of solvents, the dielectric constant alone was found not to be a direct measure of interaction in an extraction process concerning solvation behavior of the used diluents. On the other hand, empirical parameter of the polarity of solvents ( $E_{\text{T}(30)}$ ) was found to be more precise for studying the influence of diluents polarity on

the extraction rate. This empirical parameter is assumed to be a more precise measure of a solvent polarity than the dielectric constant since it considers all intermolecular forces acting in a liquid.<sup>(13)</sup> In the present study correlation between D-values and some physico-chemical properties of the used organic diluents indicates that the values of  $\log D_{Te}$ , generally increase with increasing  $E_{T(30)}$  giving straight lines in all cases. Since, this parameter indicates the polarity of a diluent, the larger the value of  $E_{T(30)}$  of a diluent, the greater is its polarity, solvation power and hence the extraction of the complexes formed in aqueous phase into organic phase. This explains the relatively high  $D_{Te}$  value in the case of nitrobenzene and chloroform. The deviation in the case of chloroform from linearity in some cases may be attributed to stronger intermolecular forces than between solvent molecules and the extracted complex.

Other parameter that may have influence on the extraction of metal complexes in organic diluents is "solubility parameter,  $\delta$ ". This parameter is proposed to be a useful concept for describing the forces responsible for various properties of the liquids. Collectively, these forces are known as the cohesive forces.<sup>(11)</sup> These forces are due to dispersion, dipole-dipole and hydrogen bonding interactions. According to Hildebrand et al.<sup>(15)</sup>

The solubility parameter  $\delta$  has contribution from the dispersion  $\delta_d$ , polar (dipole-dipole)  $\delta_p$  and hydrogen bonding  $\delta_h$  components. These components are related together by the following equation:

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$$

Correlation between  $\delta$  and efficiency of metal complexes extraction, has been illustrated in other work.<sup>(16)</sup> The correlations between  $\log D_{Te}$  and the value of water solubility W% in the investigated organic solvents shows a linear relationship. There are some deviations in the case of  $CCl_4$  and nitrobenzene. In the case of nitrobenzene, this deviation is much pronounced for the extraction from HBr and HI. This may be explained by the competition between water molecules and extracted Te species for the organic phase. On the other hand, the positive deviation in the extraction by  $CCl_4$  in some cases may be attributed to a proper covalence in the bonds of the extracted Te species. The relations between  $\log D$  and the polarizability index  $\pi$  of the used organic

diluents shows the same deviation from linearity in case of nitrobenzene, chloroform and  $\text{CCl}_4$ . However, Frazier and Wai<sup>(12)</sup>; while studying the extraction of some lanthanides; have found that  $\log D$  values are correlated to the polarizability index by the following equation:

$$\pi = \log D - n \log S_{\text{H}_2\text{O}}$$

Where,  $S_{\text{H}_2\text{O}}$  represents the solubility of water in the solvent.

Extraction of Te(IV) is also studied from aqueous solutions of HCl, HBr and  $\text{HNO}_3$  at different concentrations using the solvents 20 V% TOA, 20 V% aliquate and 30 V% TBP in xylene. In all cases straight lines are obtained, however the extraction of Te from  $\text{HNO}_3$  with the three investigated solvents is considerably low at all acid concentrations. This behavior is similar to the adsorption of Te on the anion exchanger Dowex-1.<sup>(17)</sup> Slope analysis in the case of HCl and HBr gives value of 6 in all cases indicating that 6 halide ions are participating in the formation of the extracted complex in all cases.

The extracted species of Te(IV) with the used organic diluents have to be neutral species and may be similar to that in the case of TBP extraction.

The extraction of iodine with nitrobenzene is also studied from solutions of HI. The extraction of iodine is very slight at low acid concentration, consequently good extraction from Te is possible which is useful for application in radiochemistry for separation of  $^{131}\text{I}$ , e.g. from its parent  $^{131}\text{Te}$ .

### Conclusion

The distribution ratio for the extraction of Te(IV) from the studied media, i.e. HCl, HBr, HI,  $\text{HNO}_3$ , oxalic and citric acids with seven different organic diluents is dependent on the polarity, solubility parameters and polarizability index of organic diluents as well as on the solubility of water in the organic solvent.. Te(IV) is good extracted in some systems. Separation of Te and I is good in some of the investigated system.

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